

Entangled-Photon Virtual-State Spectroscopy

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A new form of absorption spectroscopy is introduced in which the energy levels and matrix elements of *virtual-state* transitions in a medium are determined by the use of continuous-wave degenerate entangled photons without varying their wavelengths. Extractable spectroscopic information is embedded in the entangled-photon absorption cross section when measured over a range of entanglement and interbeam-delay times. This technique exploits the fundamental quantum interference that arises during the interaction of an entangled quantum state with a quantum system. [S0031-9007(98)05928-6]

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Since two-photon absorption was first described by Maria Göppert-Mayer in 1931 [1], two-photon spectroscopy has become an invaluable tool in the armamentarium of spectroscopic techniques [2]. In this Letter we show that the use of a nonclassical light source comprising entangled-photon pairs empowers two-photon spectroscopy in a remarkable and unanticipated way: It permits the extraction of information about the virtual states that contribute to the two-photon excitation, *including states whose energies exceed that of the initial-to-final state transition*. Another salutatory feature of the technique is that it is implemented by carrying out continuous-wave absorption measurements without changing the wavelength of the source. Entangled-photon virtual-state spectroscopy [3] therefore differs significantly from other spectroscopic techniques, including those that rely on other types of nonclassical light sources [4,5] or pulsed coherent excitations [6,7].

Entanglement describes a composite quantum system whose state cannot be factored into a product of single-particle states and thereby has no classical analog [8]. It is manifested by the potential to exhibit correlations that cannot be obtained with classical systems. Entangled-photon pairs exhibit quantum interference via fourth-order coincidence measurements—for example, by the use of an interferometer and a pair of photon-counting detectors [8]. The two-photon absorption process in an atom or molecule automatically serves as such a coincidence detector [9] and therefore displays quantum interference which, as we will show, can reveal spectroscopic information about an absorbing medium.

Entangled-photon generation.—Entangled-photon pairs are readily generated by spontaneous parametric down-conversion, a second-order nonlinear optical process [10], as illustrated in Fig. 1(a). Within the crystal, coherent pump photons are spontaneously down-converted into pairs of photons (the signal and idler beams) in a quantum process such that energy and momentum are conserved (phase-matching). Entangled-photon pairs are described by the twin state $\int \int d\mathbf{k}_1 d\mathbf{k}_2 \psi(\mathbf{k}_1, \mathbf{k}_2) |\mathbf{k}_1, \mathbf{k}_2\rangle$ where $\mathbf{k}_{1,2}$ are the signal and idler wave vectors, respectively, and

$\psi(\mathbf{k}_1, \mathbf{k}_2)$ is a nonseparable function that depends on the phase-matching conditions [8]. The twin photons are created within an entanglement time T_e and within an entanglement area A_e of each other; these quantities represent the widths of the fourth-order temporal- and spatial-coherence functions, respectively [11,12].

The entanglement time T_e can be tuned over a relatively broad range (an order of magnitude can be readily achieved) by using a variety of methods that depend on the system configuration. With type-I (parallel-polarized pair) phase matching, for example, focusing the pump beam changes its width and therefore serves to vary T_e [11]. With type-II (orthogonally polarized pair) phase matching, T_e is linearly proportional to the crystal length [12] so that a suitably matched set of wedge-shaped down-conversion/compensation crystals might be used. More simply, variable-bandwidth optical filters inserted before the sample can serve this purpose with either type-I or type-II down-conversion.

Entangled-photon absorption with interbeam delay.—The entangled-photon absorption rate R_e is linearly dependent on the incident photon-flux density ϕ so that $R_e = \sigma_e \phi$ where σ_e is the cross section for entangled light [13–15]. We have calculated the expression for σ_e when an adjustable time delay τ is optically introduced into one of the photon paths; this will enable us to

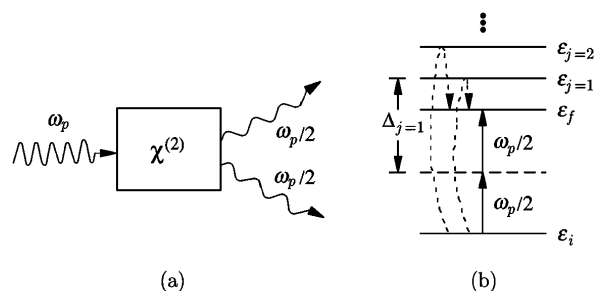


FIG. 1. Illustrations of degenerate entangled-photon-pair (a) generation by spontaneous parametric down-conversion in a nonlinear crystal with second-order susceptibility $\chi^{(2)}$ and (b) absorption in a model material system with transitions involving virtual states (dashed curves).

carry out entangled-photon spectroscopy. We assume that the pump is monochromatic with frequency ω_p and the down-converted entangled photons are degenerate with central wave-packet frequencies $\omega_1^0 = \omega_2^0 = \omega_p/2$. The medium is characterized by an initial energy state $|\varepsilon_i\rangle$, a final state $|\varepsilon_f\rangle$ with linewidth κ_f , and a collection of virtual states $|\varepsilon_j\rangle$ [see Fig. 1(b)].

Simultaneous absorption of the entangled-photon pair can occur only within a rectangular window of width T_e , requiring that the path delay is $|\tau| < T_e$. The interaction of the twin state with the quantum system can then be evaluated using standard second-order perturbation methods. The entangled-photon cross section $\sigma_e(T_e, \tau)$ is calculated to be

$$\sigma_e(T_e, \tau) = \frac{\pi \omega_p^2}{16A_e T_e} \delta(\varepsilon_f - \varepsilon_i - \omega_p) s(T_e, \tau), \quad (1)$$

with

$$s(T_e, \tau) = \left| \sum_j A_j \{ 2 - \exp[-i\Delta_j(T_e - \tau)] - \exp[-i\Delta_j(T_e + \tau)] \} \right|^2. \quad (2)$$

$$s(T_e, \tau) = 4 \sum_{j,k} A_j A_k^* - 2 \sum_{j,k} A_j A_k^* \{ \exp(-i\Delta_j T_e) [\exp(i\Delta_j \tau) + \text{c.c.}] + \exp(i\Delta_k T_e) [\exp(i\Delta_k \tau) + \text{c.c.}] \} + \sum_{j,k} A_j A_k^* \exp[-i(\Delta_j - \Delta_k)T_e] (\{ \exp[i(\Delta_j + \Delta_k)\tau] + \text{c.c.} \} + \{ \exp[i(\Delta_j - \Delta_k)\tau] + \text{c.c.} \}). \quad (3)$$

The spectroscopic information resident in this equation can be extracted by means of a two-dimensional Fourier analysis which exposes the unknown frequencies Δ_j as well as the transition matrix elements inherent in the coefficients A_j .

For a single *fixed* value of T_e , the cross section $\sigma_e(T_e, \tau)$ as a function of τ contains spectral components at the frequencies 0, $\pm\Delta_j$, and $\pm(\Delta_j \pm \Delta_k)$. The amplitudes of these components take the form of a series of products of the $\{A_j\}$. In this case, without prior knowledge of the energy levels of the sample, it is not possible to determine both the Δ_j and the associated A_j . However, for a cross section with a few simple absorption features, it may suffice to evaluate Eq. (3) or its Fourier transform at a small number of suitably chosen values of T_e .

Another method that avoids the use of a two-dimensional Fourier transform involves averaging $s(T_e, \tau)$ in Eq. (3) over a range of values of T_e , which removes all terms in the second summation and all terms for which $j \neq k$ in the third summation, so that Eq. (3) simplifies to

$$\bar{\sigma}(\tau) = 4 \sum_{j,k} A_j A_k^* + \sum_j |A_j|^2 [2 + \exp(-i2\Delta_j \tau) + \exp(i2\Delta_j \tau)]. \quad (4)$$

The energy mismatch is denoted $\Delta_j = \varepsilon_j - \varepsilon_i - \omega_p/2$, the coefficients are $A_j = D_j/\Delta_j$, and the transition matrix elements are $D_j = \langle \varepsilon_f | d | \varepsilon_j \rangle \langle \varepsilon_j | d | \varepsilon_i \rangle$ with material electric-dipole moments d ; units are chosen such that $\hbar = c = 1$. We have assumed that the virtual-state linewidths are negligible, which is valid if they, along with the entanglement time, are sufficiently small [14]. The two terms with $\pm\tau$ arise because of the equivalence of one photon being advanced or delayed relative to the other. Equations (1) and (2) include the full phase-path dependence of entangled-photon absorption so that they are sensitive to the relative phases of the contributing intermediate dipole-allowed transitions of the medium. They comprise the principal results of this paper; when $\tau = 0$, they reduce to the previously derived expression [14].

Entangled-photon virtual-state spectroscopy.—It is evident from the presence of the quantity Δ_j in Eq. (2) that the entangled-photon absorption cross section contains information relating to the virtual-state energy levels of the medium, as shown in Fig. 1(b) (ε_i and ω_p are known). From the form of Eq. (2), it is clear that the dependence of $s(T_e, \tau)$ can be viewed as a sum of harmonic functions of T_e and τ with various frequencies $\pm\Delta_j$. This can be explicitly shown by expanding $s(T_e, \tau)$:

This result is valid provided that the range of T_e is much greater than the inverse of the smallest frequency difference $|\Delta_j - \Delta_k|$ to be resolved ($j \neq k$). For data collected within a range $T_e^{(\min)} < T_e < T_e^{(\max)}$ (the minimum and maximum values are designated by the use of the superscripts min and max, respectively) and with sufficiently small increments in T_e , the weighted-and-averaged cross section $\bar{\sigma}_e(\tau)$ can be written in the form of an integral

$$\bar{\sigma}_e(\tau) = \frac{1}{T} \int_{T_e^{(\min)}}^{T_e^{(\max)}} \sigma_e(T_e, \tau) T_e dT_e \approx \frac{\pi \omega_p^2}{16A_e} \delta(\varepsilon_f - \varepsilon_i - \omega_p) \bar{s}(\tau), \quad (5)$$

where the range of entanglement times $T = T_e^{(\max)} - T_e^{(\min)} \gg 1/|\Delta_j - \Delta_k|$ for all $j \neq k$, and the factor T_e is included in the integrand to cancel the $1/T_e$ dependence of the cross section in Eq. (1).

Since $\bar{\sigma}_e(\tau) \propto \bar{s}(\tau)$, its spectrum has components at the frequencies $2\Delta_j$ with magnitudes $|A_j|^2$. A straightforward Fourier analysis of $\bar{\sigma}_e(\tau)$ therefore provides the unknown energy levels of the system ε_j together with the unknown strengths of the transition matrix elements $|D_j|$. It is, in principle, also possible to determine the phases of the transition matrix elements. Multiplying $s(T_e, \tau)$ in Eq. (3) by the harmonic function $\exp[i(\Delta_j - \Delta_k)T_e]$ prior to

the operation of averaging over T_e results in an average proportional to $A_j A_k^*$. With the magnitudes $|A_j|^2$ already determined, selecting different values of $\Delta_j - \Delta_k$ permits the relative phases of A_j and A_k , and thereby the phases of all of the transition matrix elements (up to a constant), to be extracted.

Because $\overline{\sigma}_e(\tau)$ is associated with a minimum range of values $|\tau| < T_e^{(\min)}$, the best possible spectral resolution is determined by $1/T_e^{(\min)}$. The spectral range is determined by the number of sampling points in the range of τ . Since $|A_j| \propto 1/|\Delta_j|$ the accuracy with which energy-level information can be obtained diminishes with increasing virtual-state energy. Furthermore, a more stringent restriction on the spectral range will be imposed by any edge smoothing of the rectangular time window.

The physical origin of this ability to obtain information about the virtual-state spectrum arises from the composition of the entangled-photon absorption cross section as a coherent summation of two-photon interaction terms. The absorption depends on both the arrival-time spread T_e and on the relative phase of the photons in each pair, which depends on the delay time τ . Therefore, the absorption amplitudes for each possible path, from the initial state through each intermediate state to the final state, vary distinctively with both parameters. Variation in either T_e or τ alters the phases of the contributions in Eqs. (2) and (3) and leads to nonmonotonic variations in the absorption cross section. Our technique exploits this dependence.

Thus, entangled-photon virtual-state spectroscopy is distinctively different from spectroscopic techniques that make use of other kinds of nonclassical light sources, such as photon-number-squeezed [4] or quadrature-squeezed [5] light. Our method is also to be distinguished from Fourier techniques that make use of pulsed coherently controlled optical transitions [6,7]. These methods lead to a cross section in which intermediate levels do not appear as coefficients of a time-dependent quantity, as they do in Eq. (2); hence, intermediate-level information cannot be accessed.

Example: Atomic hydrogen.—We explicitly demonstrate the implementation of entangled-photon virtual-state spectroscopy by carrying out numerical simulations with the exactly calculable case of the $1S$ - $2S$ two-photon transition in atomic hydrogen. This transition takes place via intermediate P states: $1S \rightarrow 2P \rightarrow 2S$, $1S \rightarrow 3P \rightarrow 2S$, etc., which are connected to the S states by real-valued electric-dipole matrix elements. The hydrogen-atom energy levels are $\varepsilon_n = -13.6/n^2$ eV (13.6 eV is the Rydberg constant) where $n = 1, 2, 3, \dots$, the zero of energy ($n = \infty$) corresponds to ionization, and $\Delta_n = \varepsilon_n + 8.50$ eV. We assume the use of a monochromatic pump with $\omega_p = \varepsilon_f - \varepsilon_i$ [see Fig. 1(b)] and parallel-polarized entangled photons with $A_e = 10^{-6}$ cm². We further assume that the $2S$ state is Lorentzian broadened with a natural lifetime $1/\kappa_f = 122$ ms [16] and evaluate the cross sections using ten principal quantum numbers (the final-state lifetime is accounted for in our calculation

by multiplying the cross section by the linewidth function and integrating over the final-state energy).

Information pertaining to the values of the energy levels can be obtained with a single value of T_e , as demonstrated in Fig. 2. Here, the full spectrum includes the energy levels along with their sums and differences in accordance with Eq. (3). The use of one or a few values of T_e , for which the averaging is insufficient to eliminate the peaks at $\pm(\Delta_j \pm \Delta_k)$, requires that an appropriate window be used to isolate the energy levels of the medium. For a system chosen such that $2\Delta_j^{(\min)} > \Delta_j^{(\max)}$, the window encompasses $\Delta_j^{(\min)}$ and $2\Delta_j^{(\min)}$. Hence, in this case *a priori* knowledge of the medium's lowest lying virtual-state energy level, or a more sophisticated data analysis technique, is required for proper interpretation of the data. Particular values of T_e affect the heights of the peaks but not their locations.

We now demonstrate the implementation of the technique of averaging the cross section over a range of entanglement times to obtain part of the virtual-state spectrum. The result of evaluating Eq. (5) for the $1S$ - $2S$ atomic hydrogen transition, after normalizing and carrying out the Fourier transform, is presented in Fig. 3. Both the energy levels and transition matrix elements, which correspond to the heights of the peaks, emerge clearly. The virtual-state energy levels are determined from the locations of the peaks at -3.40 , -1.50 , and -0.85 eV. These three values are readily identified with $n = 2, 3$, and 4 corresponding to the $2P, 3P$, and $4P$ states, respectively. Values of the transition matrix elements obtained from the heights of the peaks correspond to actual values. The total incident entangled-photon-pair energy ($2\varepsilon_i = 10.2$ eV) is such that, if the light were classical, energy levels higher

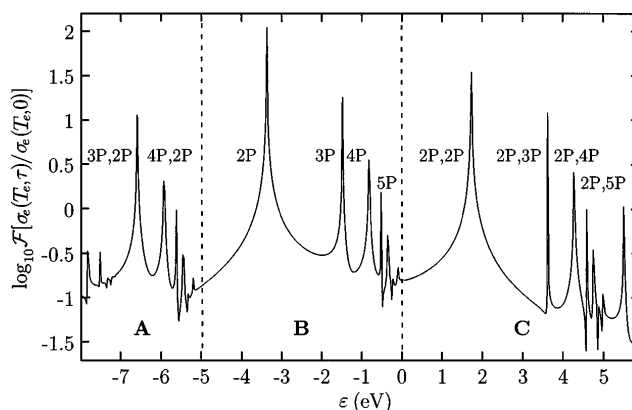


FIG. 2. Fourier transform of the normalized atomic hydrogen $1S$ - $2S$ cross section $\mathcal{F}[\sigma_e(T_e, \tau)/\sigma_e(T_e, 0)]$ as a function of energy ε using a fixed entanglement time $T_e = 2002$ fs and an interbeam delay time range $0 \leq \tau \leq 1000$ fs with increments $\delta\tau = 0.5$ fs. The dashed lines provide an indication of the boundaries within which the spectral components are dominated by terms with **A**: $\pm(\Delta_j - \Delta_k)$, **B**: $\pm\Delta_j$, and **C**: $\pm(\Delta_j + \Delta_k)$; some of the intermediate-state energy peaks are labeled by the atomic levels corresponding to Δ_j and Δ_k .

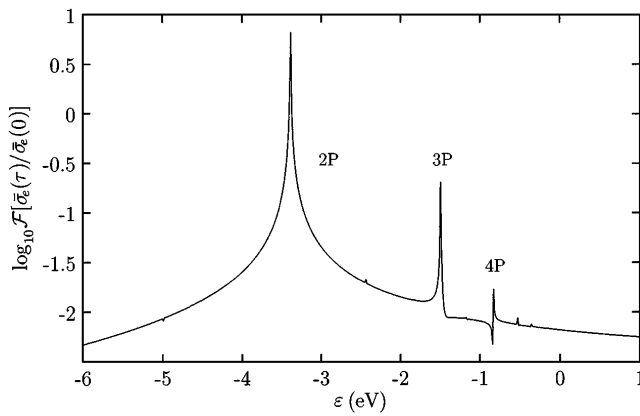


FIG. 3. Fourier transform of the normalized weighted-and-averaged atomic hydrogen 1S-2S cross section $\mathcal{F}[\bar{\sigma}_e(\tau)/\bar{\sigma}_e(0)]$ as a function of energy ε using an entanglement-time range $1001 < T_e \leq 2001$ fs and an interbeam delay-time range $0 \leq \tau \leq 1000$ fs with increments $\delta T_e = \delta \tau = 0.5$ fs.

than -3.4 eV ($2P$) could not be accessed. The fact that the $3P$ and $4P$ levels are evident in Fig. 3 provides evidence of a most unusual capability of entangled-photon virtual-state spectroscopy.

Generalizations.—Although our formulation of entangled-photon virtual-state spectroscopy is illustrated by means of a medium with discrete energy levels, it is applicable for arbitrary media, including those with continuous absorption bands such as semiconductors. The method is readily generalized to entangled N -photon virtual-state spectroscopy where $N = 2, 3, 4, \dots$ [17]. Furthermore, the use of nondegenerate twin photons and other types of pair states, such as those generated by means of stimulated down-conversion in optical parametric amplifiers and oscillators, may provide useful versions of entangled-photon spectroscopy as well. Moreover, the interaction of entangled-photon pairs with *pairs of electrons*, such as those in a helium atom, offers access to the spectroscopic behavior of systems with joint entangled excitations. Finally, since entangled-photon virtual-state spectroscopy is based on the characteristics of the fundamental quantum interference that arises during the interaction of an entangled quantum state with a quantum system, it is likely to be applicable for nonphotonic entangled probes and their interaction with nonatomic quantum systems as well. One example of potential interest is the interaction of an entangled atomic state [18] with a quantum cavity [19] to determine the cavity modes.

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